



# The Use of Electrolyte Additives to Improve the High Temperature Resilience of Li-Ion Cells

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# Objective

- The objective to identify lithium-ion electrolytes, which will lead to Li-ion cells with a wide operational temperature range (+60 to -60°C),
- Develop Li-ion electrolytes which result in cells that display improved high temperature resilience.

# Approach

- Identify capacity fade and impedance growth mechanisms of lithium-ion cells subjected to high temperature storage and cycling.
- Develop multi-component electrolyte solutions incorporating the addition of promising electrolyte additives which are targeted at improving the robustness of the electrode surface films (SEI promoters) and improving the inherent thermal stability of the electrolytes (thermal stabilizing agents).
- Evaluate candidate electrolyte formulations in experimental lithium-ion cells (i.e., MCMB-LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> with lithium metal reference electrodes) in terms of their electrical and electrochemical properties
- Determine the influence of electrolyte type upon the degradation mechanisms of the experimental lithium-ion cells after being subjected to high temperature, by performing periodic electrochemical analysis.
- Perform ex-situ analysis of electrode sample retrieved from cells after high temperature exposure (Univ. of Rhode Island activity).





# High Temperature Resilient Li-Ion Electrolytes

## Electrolyte Development: Approach/Background

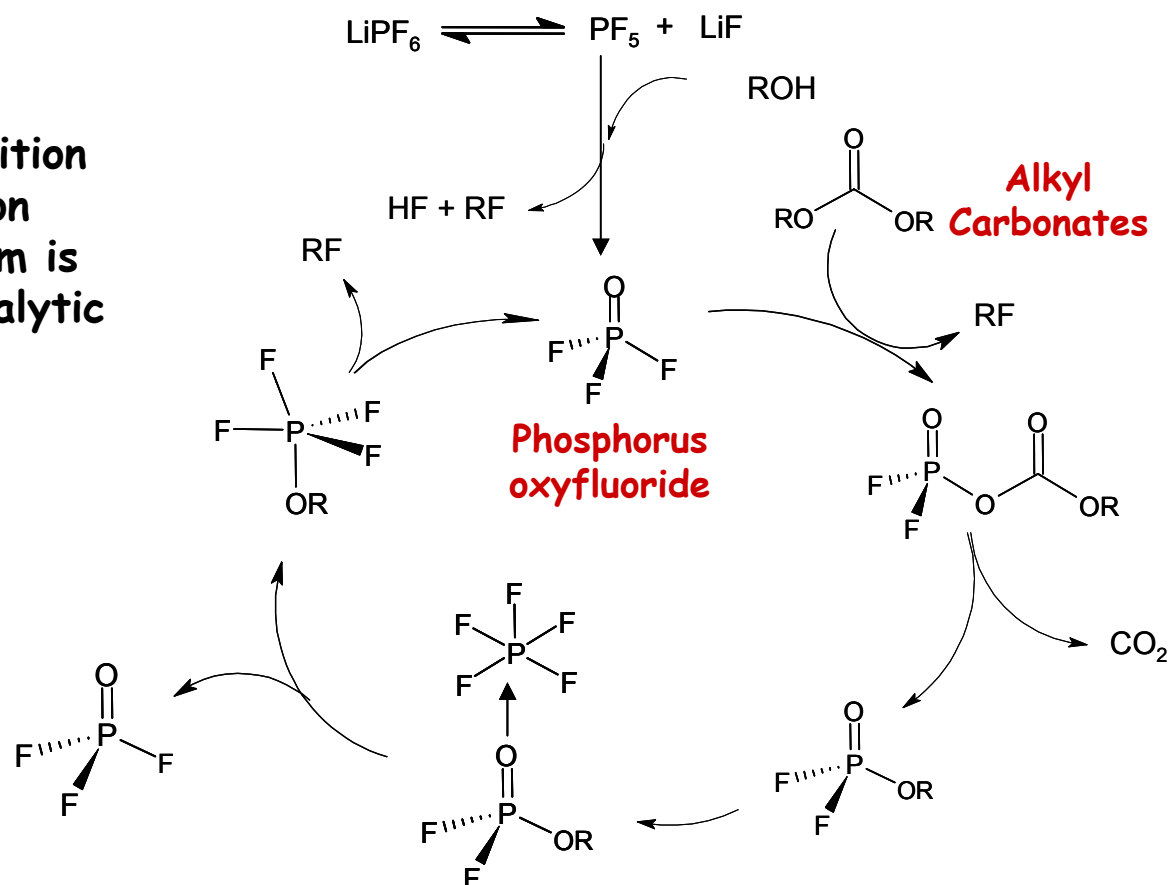
- *Effect of high temperature exposure on Li-ion cells*
  - High temperature exposure is known to lead to irreversible capacity loss and impedance growth, especially at temperatures  $> 40^{\circ}\text{C}$ .
  - The performance losses are more dramatic when the cells are maintained at high SOC and/or cycled to high potential.
- *Potential degradation modes at high temperatures*
  - The formation of resistive surface films on the carbon anodes, indirectly due to the decomposition of the electrolyte.
  - Increase in cathode impedance and decrease in cathode  $\text{Li}^+$  kinetics, due to loss of inter-particle connection and possibly formation of surface films.
  - Thermal and/or electrochemical decomposition of electrolyte.
  - Relative contribution of potential degradation modes chemistry dependant.
- *Potential mitigation strategies*
  - Operational protocols (i.e., limiting the SOC at high temperature).
  - Modifying electrode chemistries.
  - Modifying electrolyte composition:
    - *Use of thermally stable electrolyte salts*
    - *Use of electrolyte additives to stabilize  $\text{LiPF}_6$ -based solutions*



# High Temperature Resilient Li-Ion Electrolytes

## Background - Proposed Mechanism of Thermal Decomposition

Decomposition  
Reaction  
Mechanism is  
Auto-Catalytic



The addition of dimethyl acetamide and N-methyl pyrrolidinone to the baseline low temperature electrolyte is intended to complex the reactive  $\text{PF}_5$  Lewis acid generated above.

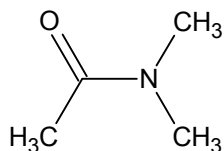


# High Temperature Resilient Li-Ion Electrolytes

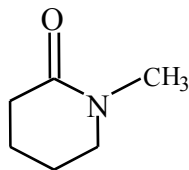
## Approach

- The following electrolyte additives were investigated to (a) improve the thermal stability of the electrolyte itself and to (b) produce desirable protective surface films on the anode (and the cathode) to enhance the high temperature resilience.

Additives envisioned to complex with the Lewis acidic  $\text{PF}_5$  species liberated

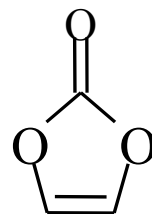


N,N-Dimethyl  
Acetamide  
(DMAc)

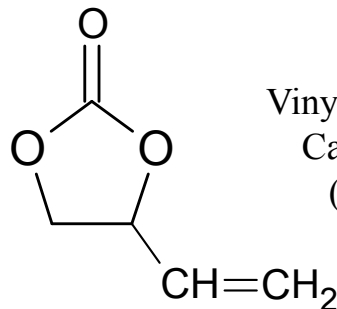


N-Methyl  
Pyrrolidinone  
(NMP)

Additives targeted at forming robust, protective SEI layers on the electrode surfaces



Vinylene  
Carbonate  
(VC)



Vinyl Ethylene  
Carbonate  
(VEC)





## Experimental MCMB-LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> Carbon Cells

### Electrolytes Selected for Evaluation in Experimental Cells

1.0 M LiPF <sub>6</sub>	EC+DEC+DMC (1:1:1 v/v %)	(Baseline)
1.0 M LiPF <sub>6</sub>	EC+DEC+DMC (1:1:1 v/v %)	+ 1 % DMAc
1.0 M LiPF <sub>6</sub>	EC+DEC+DMC (1:1:1 v/v %)	+ 3 % DMAc
1.0 M LiPF <sub>6</sub>	EC+DEC+DMC (1:1:1 v/v %)	+ 10 % DMAc
1.0 M LiPF <sub>6</sub>	EC+DEC+DMC (1:1:1 v/v %)	+ 3 % NMP
1.0 M LiPF <sub>6</sub>	EC+DEC+DMC (1:1:1 v/v %)	+ 1.5 % VC
1.0 M LiPF <sub>6</sub>	EC+DEC+DMC (1:1:1 v/v %)	+ 1.5 % VEC



- MCMB Carbon-LiNiCoO<sub>2</sub> Cells
- 400-450 mAh Size Cells
- All Cells equipped psuedo Li metal reference electrodes
- Flooded electrolyte design (cylindrical cells)

### Techniques Used to Study the Performance Characteristics

- Charge/discharge behavior at various temperatures
- Electrochemical Impedance Spectroscopy (EIS)
- DC Polarization Techniques





## Formation Cycling at Room Temperature

- Experimental lithium-ion cells (MCMB-LiNiCoO<sub>2</sub>) fabricated with low temperature electrolytes containing various additives.

Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreversible Capacity (1st Cycle)	Coulombic Efficiency (1st Cycle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreversible Capacity (1st-5th Cycle)	Coulombic Efficiency (5th Cycle)
1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %)	0.4548	0.3890	0.066	85.52	0.3863	0.3759	0.1155	97.30
1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 1 % DMAc	0.4492	0.3861	0.063	85.95	0.3831	0.3770	0.0975	98.40
1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 3 % DMAc	0.4496	0.3837	0.066	85.33	0.3874	0.3739	0.1261	96.51
1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 10 % DMAc	0.4561	0.3868	0.069	84.80	0.3845	0.3757	0.1123	97.71
1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 3 % NMP	0.4854	0.4139	0.072	85.25	0.4136	0.4053	0.1118	97.99
1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 1.5 % VC	0.4998	0.4271	0.073	85.45	0.4255	0.4183	0.1178	98.30
1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 1.5 % VEC	0.4662	0.3861	0.080	82.82	0.3789	0.3658	0.1421	96.53

Initial formation of cells containing electrolytes with the various additives displayed comparable behavior to the baseline cells, with minimal increase in the irreversible capacity.





## Performance of High Temperature Resilient Li-Ion Electrolytes

### Summary of Discharge Performance After High Temperature Storage

			1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %)		1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 1 % DMAc		1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 2 % DMAc		1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 3 % DMAc		1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 10 % DMAc	
			mAh	% of Initial	mAh	% of Initial	mAh	% of Initial	mAh	% of Initial	mAh	% of Initial
Prior to Storage Tests	Temp = 20°C	25 mA	365.43	100.00	373.26	100.00	351.97	100.00	360.44	100.00	373.18	100.00
		50 mA	361.92	99.04	368.75	98.79	343.61	97.63	353.56	98.09	368.97	98.87
		100 mA	355.46	97.27	359.78	96.39	331.10	94.07	341.00	94.61	356.65	95.57
	Temp = - 20°C	25 mA	326.08	89.23	325.56	87.22	299.97	85.23	304.03	84.35	327.63	87.79
		50 mA	309.37	84.66	302.78	81.12	286.12	81.29	290.14	80.50	298.11	79.88
		100 mA	294.12	80.49	284.01	76.09	265.53	75.44	264.96	73.51	277.46	74.35
After 10 Days Storage at 55°C	Temp = 20°C	Residual	188.09	51.47	283.94	76.07	186.08	52.87	224.99	62.42	127.59	34.19
		25 mA	217.28	59.46	324.12	86.83	250.22	71.09	290.16	80.50	270.73	72.55
		50 mA	211.79	57.96	317.91	85.17	242.18	68.81	283.84	78.75	254.23	68.12
	Temp = - 20°C	100 mA	202.33	55.37	304.44	81.56	227.20	64.55		0.00	227.35	60.92
		25 mA *	184.72	50.55	279.27	74.82	197.77	56.19	232.53	64.51	216.65	58.05
		25 mA	157.49	43.10	264.76	70.93	149.38	42.44	189.21	52.50	169.01	45.29
		50 mA	139.56	38.19	247.35	66.27	111.26	31.61	154.74	42.93	141.51	37.92
		100 mA	85.01	23.26	203.80	54.60	52.47	14.91	85.94	23.84	76.23	20.43
		Residual	86.584	23.69	230.08	61.64	129.56	36.81	194.74	54.03	55.20	14.79
	Temp = 20°C	25 mA	108.294	29.64	245.75	65.84	163.74	46.52	233.57	64.80	136.69	36.63
		50 mA	95.408	26.11	229.12	61.38	151.55	43.06	221.00	61.31	106.64	28.58
		100 mA	79.689	21.81	202.93	54.37	131.15	37.26	201.60	55.93	74.21	19.89
After 10 Days Storage at 60°C	Temp = - 20°C	25 mA *	7.112	1.95	177.77	47.63	17.61	5.00	79.49	22.05	93.26	24.99
		25 mA	2.977	0.81	134.24	35.96	13.52	3.84	68.90	19.11	45.24	12.12
		50 mA	0.221	0.06	85.02	22.78	2.84	0.81	38.92	10.80	11.36	3.05
	Temp = 20°C	100 mA	0.039	0.01	29.54	7.91	0.04	0.01	22.05	6.12	1.18	0.32
		Residual	8.77	2.40	130.92	35.08	33.20	9.43	135.50	37.59	14.30	3.83
		25 mA	14.89	4.07	141.12	37.81	41.27	11.73	165.07	45.80	45.84	12.28
		50 mA	6.57	1.80	123.93	33.20	21.55	6.12	140.47	38.97	26.99	7.23
		100 mA	2.35	0.64	97.86	26.22	10.93	3.10	106.20	29.46	7.34	1.97
		25 mA *	0.001	0.00	40.19	10.77	0.01	0.00	15.44	4.28	4.72	1.27
After 10 Days Storage at 65°C	Temp = - 20°C	25 mA	0.001	0.00	36.18	9.69	0.01	0.00	8.61	2.39	2.33	0.62
		50 mA	0.001	0.00	8.67	2.32	0.02	0.01	2.98	0.83	0.10	0.03
		100 mA	0.002	0.00	0.05	0.01	0.02	0.01	0.08	0.02	0.06	0.02
	Temp = 20°C	Residual	8.77	2.40	130.92	35.08	33.20	9.43	135.50	37.59	14.30	3.83
		25 mA	14.89	4.07	141.12	37.81	41.27	11.73	165.07	45.80	45.84	12.28
		50 mA	6.57	1.80	123.93	33.20	21.55	6.12	140.47	38.97	26.99	7.23

- As shown in the table above, improved high temperature resilience was obtained with electrolytes containing DMAc compared to the baseline formulation.





## Performance of High Temperature Resilient Li-Ion Electrolytes

### Summary of Discharge Performance After High Temperature Storage

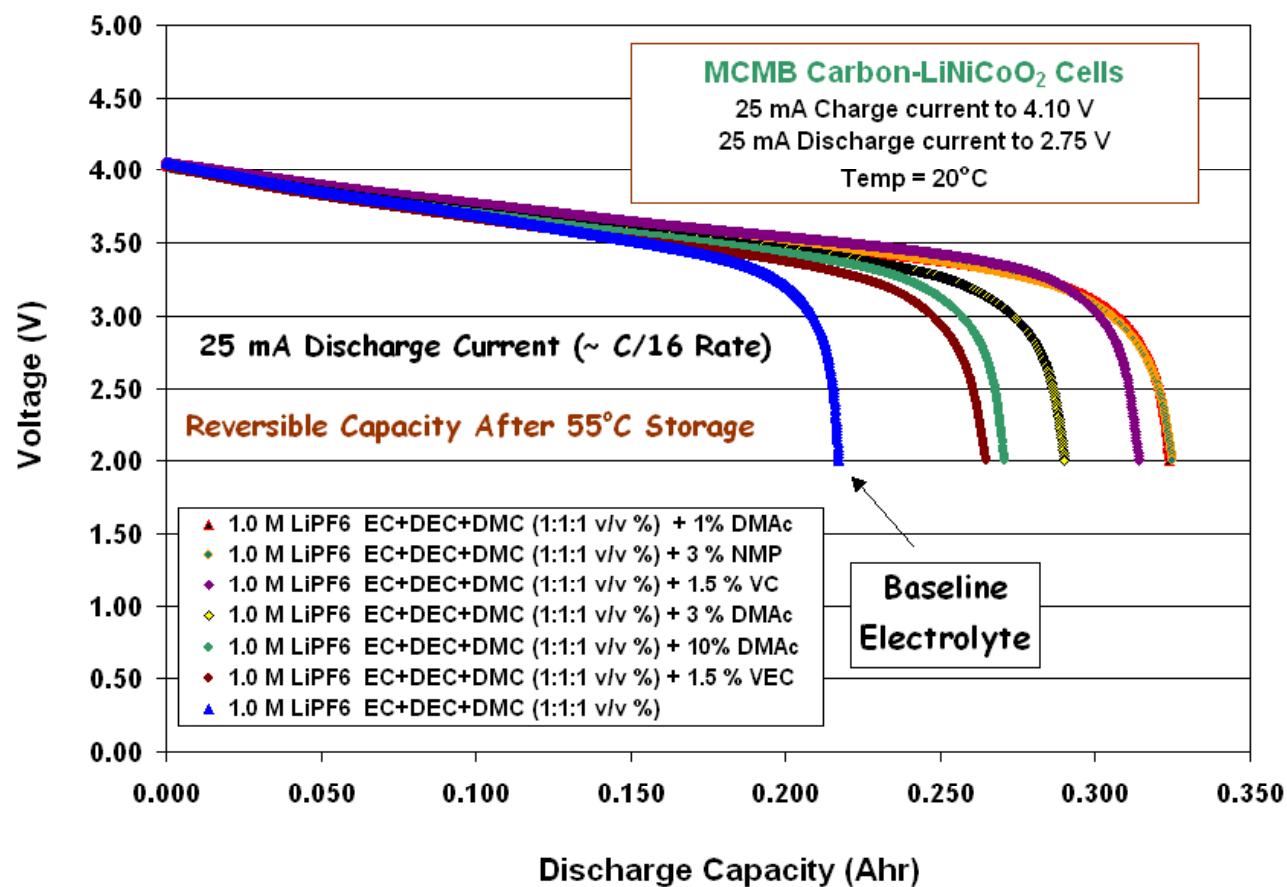
			1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %)		1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 3 % NMP		1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 1.5 % VC		1.0 M LiPF <sub>6</sub> EC+DEC+DMC (1:1:1 v/v %) + 1.5 % VEC	
			Ah	% of Initial	Ah	% of Initial	Ah	% of Initial	Ah	% of Initial
Prior to Storage Tests	Temp = 20°C	25 mA	0.3654	100.00	0.4013	100.00	0.3916	100.00	0.3509	100.00
		50 mA	0.3619	99.04	0.3940	98.19	0.3859	98.54	0.3438	97.99
		100 mA	0.3555	97.27	0.3797	94.61	0.3748	95.69	0.3286	93.66
	Temp = - 20°C	25 mA *			0.3396	84.63	0.3570	91.17	0.3030	86.35
		50 mA	0.3261	89.23	0.3213	80.07	0.3314	84.62	0.2792	79.57
		100 mA	0.3094	84.66	0.3055	76.12	0.3164	80.80	0.2667	76.02
After 10 Days Storage at 55°C	Temp = 20°C	100 mA	0.2941	80.49	0.2775	69.16	0.2953	75.40	0.2441	69.56
		Residual	0.1881	51.47	0.2809	69.99	0.3029	77.36	0.2473	70.48
		25 mA	0.2173	59.46	0.3250	80.99	0.3142	80.23	0.2648	75.48
	Temp = - 20°C	50 mA	0.2118	57.96	0.3099	77.23	0.3034	77.47	0.2499	71.24
		100 mA	0.2023	55.37	0.2833	70.60	0.2897	73.96	0.2277	64.91
		25 mA *	0.1847	50.55	0.2215	55.19	0.2788	71.19	0.2226	63.43
After 10 Days Storage at 60°C	Temp = 20°C	25 mA	0.1575	43.10	0.1699	42.35	0.2385	60.89	0.1816	51.76
		50 mA	0.1396	38.19	0.1256	31.29	0.2096	53.52	0.1494	42.59
		100 mA	0.0850	23.26	0.0600	14.94	0.1535	39.20	0.0843	24.04
	Temp = - 20°C	Residual	0.0866	23.69	0.1991	49.62	0.2096	53.52	0.1353	38.57
		25 mA	0.1083	29.64	0.2201	54.84	0.2200	56.17	0.1421	40.49
		50 mA	0.0954	26.11	0.1910	47.59	0.2045	52.21	0.1271	36.21
After 10 Days Storage at 65°C	Temp = 20°C	100 mA	0.0797	21.81	0.1455	36.27	0.1866	47.65	0.1050	29.92
		25 mA *	0.0071	1.95	0.0644	16.04	0.1614	41.22	0.0676	19.28
		50 mA	0.0030	0.81	0.0510	12.70	0.1210	30.89	0.0596	16.99
	Temp = - 20°C	100 mA	0.0002	0.06	0.0164	4.08	0.0872	22.27	0.0267	7.61
		Residual	0.0000	0.01	0.0011	0.28	0.0420	10.73	0.0052	1.48
		25 mA	0.0088	2.40	0.0665	16.58	0.1241	31.68	0.0531	15.12
After 10 Days Storage at 65°C	Temp = 20°C	50 mA	0.0149	4.07	0.0401	10.00	0.1346	34.36	0.0647	18.45
		100 mA	0.0066	1.80	0.0198	4.94	0.1235	31.53	0.0461	13.15
		25 mA *	0.0024	0.64	0.0081	2.03	0.1085	27.72	0.0042	1.21
	Temp = - 20°C	100 mA	0.0000	0.00	0.0000	0.00	0.0144	3.67	0.0014	0.40
		25 mA	0.0000	0.00	0.0000	0.00	0.0106	2.71	0.0009	0.26
		50 mA	0.0000	0.00	0.0000	0.01	0.0014	0.36	0.0000	0.01
After 10 Days Storage at 65°C	Temp = - 20°C	100 mA	0.0000	0.00	0.0001	0.02	0.0000	0.01	0.0001	0.02

- As shown in the table above, improved high temperature resilience was obtained with all of the additional additives investigated (NMP, VC, and VEC), with VC displaying the best performance.



## Performance of High Temperature Resilient Li-Ion Electrolytes

### Results of High Temperature Storage Testing (55°C Exposure)

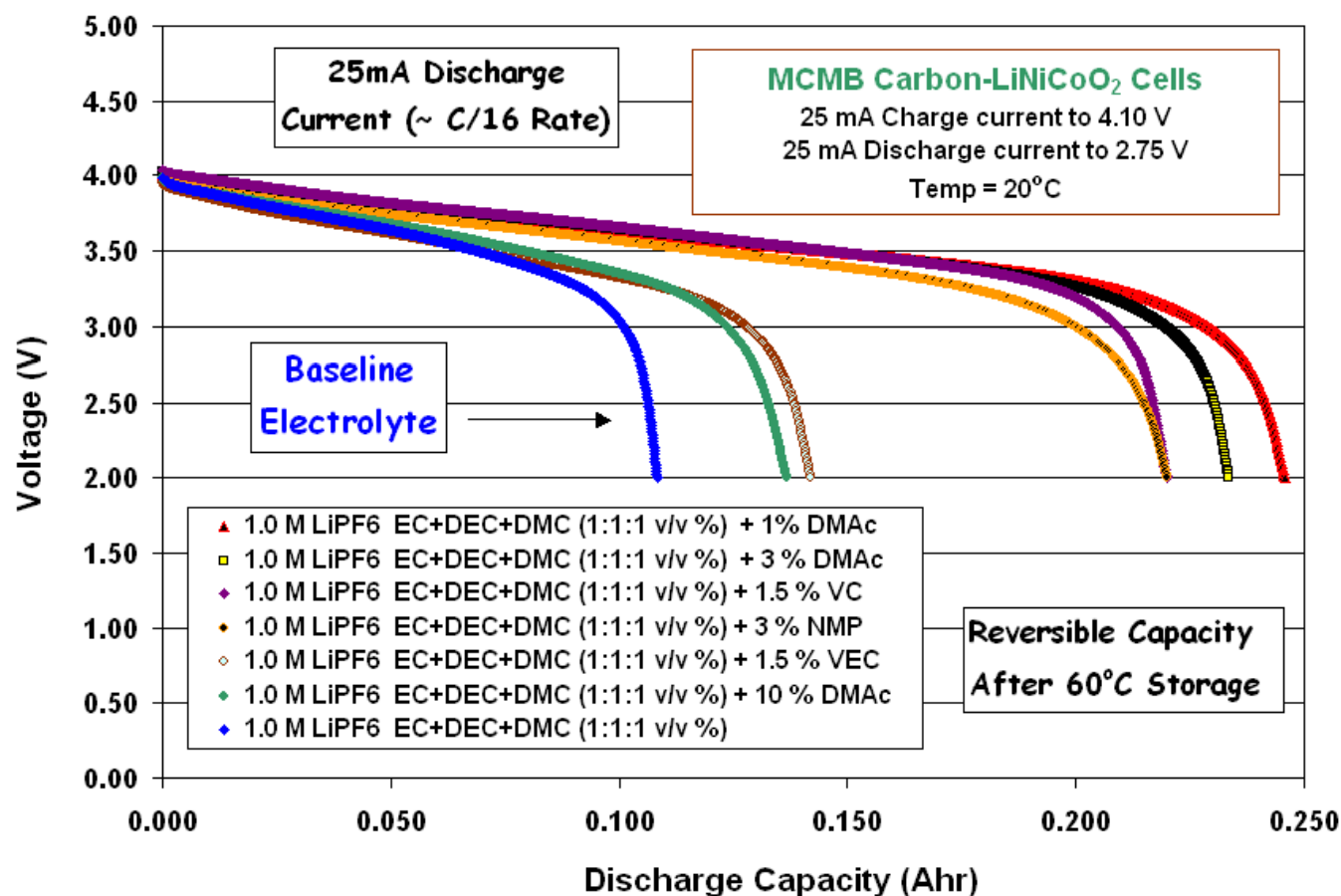


- Electrolytes with 1 % DMAc, 3 % NMP, and 1.5 %VC out-performed the baseline electrolyte when subjected to 10 days of storage at 55°C.



## Performance of High Temperature Resilient Li-Ion Electrolytes

### Results of High Temperature Storage Testing (60°C Exposure)

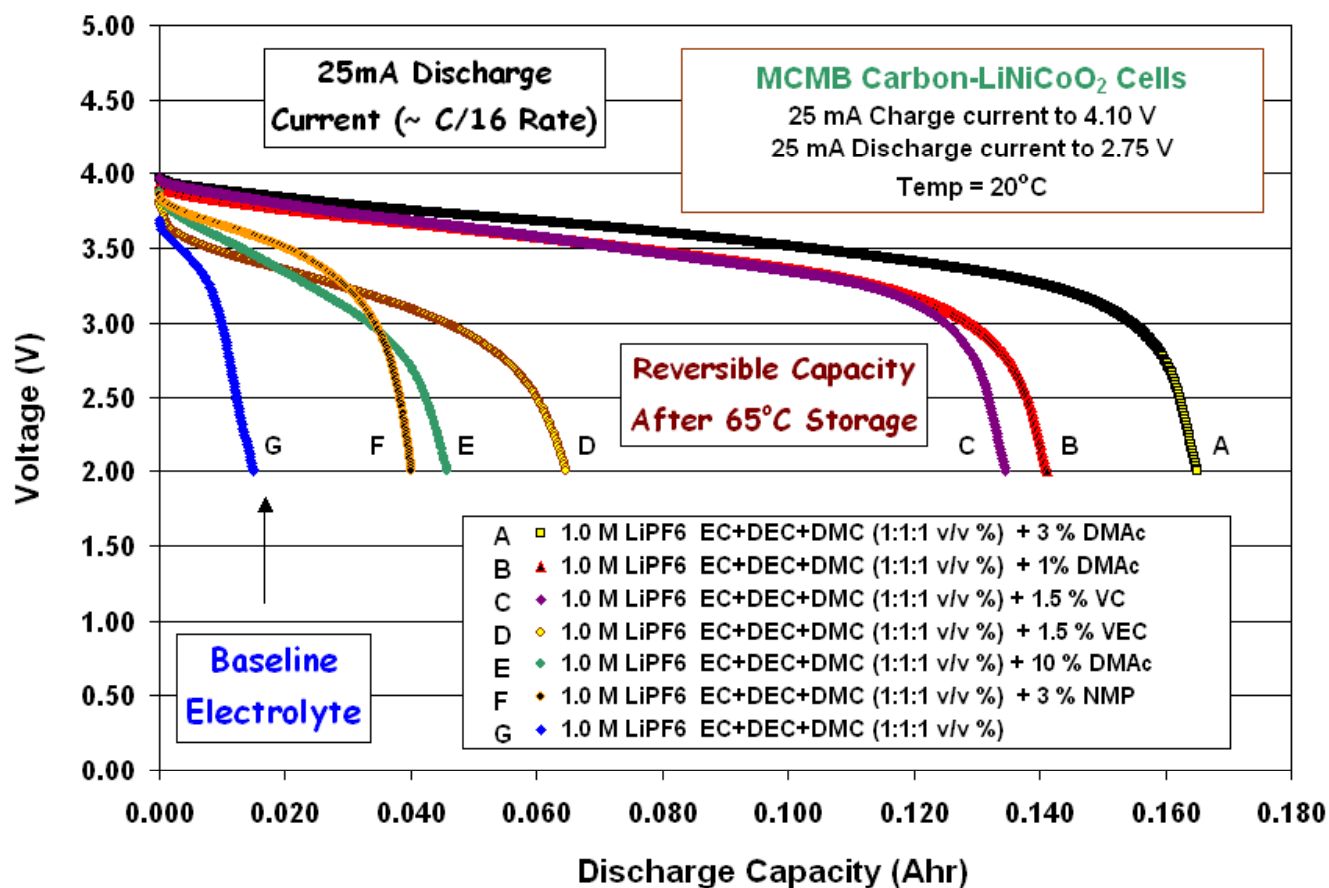


- The cell containing the electrolyte with 1 % DMAc displayed superior performance after being subjected to 10 days storage at 60°C (20 days total storage time).



## Performance of High Temperature Resilient Li-Ion Electrolytes

### Results of High Temperature Storage Testing (65°C Exposure)



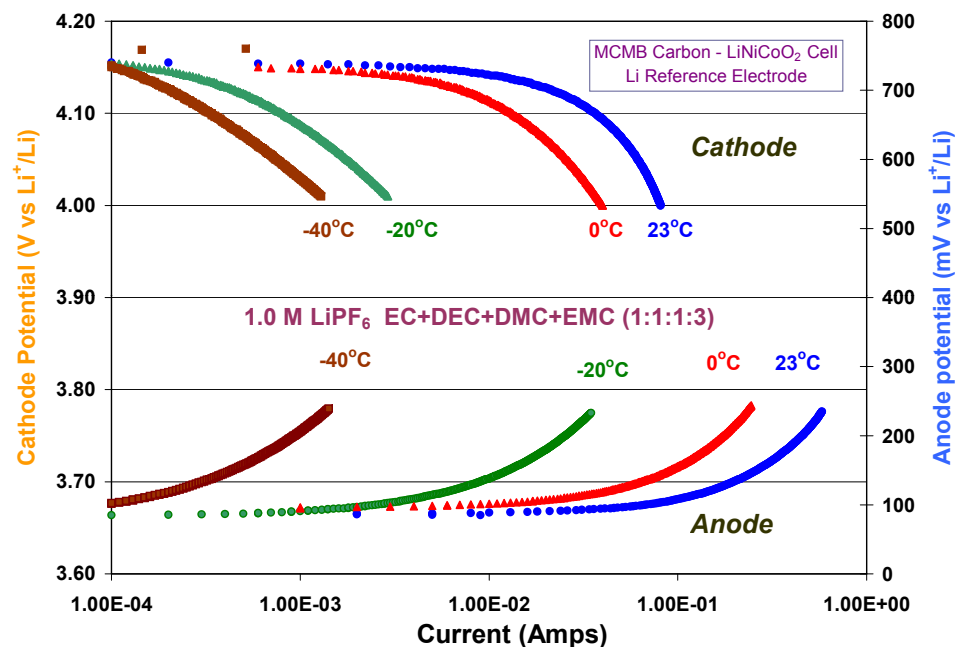
➤ The cell containing the electrolyte with 1 % DMAc and 1.5 % VC displayed superior performance after being subjected to 10 days storage at 65°C (30 days total storage time).



## Tafel Polarization Measurements of MCMB and LiNiCoO<sub>2</sub> Electrodes

### Effect of Electrolyte upon Polarization at Different Temperatures

- Tafel polarization measurements allow further insight into the kinetics of lithium intercalation/de-intercalation on MCMB anodes and LiNiCoO<sub>2</sub> cathodes in these electrolytes.
- These measurements were made at scan rates slow enough (0.5 mV/s) to provide near-steady state conditions and yet with minimal changes in the state of charge of the electrode or its surface conditions.
- The cells were tested in near full state of charge and biased over a 150 mV range.
- Both anode and cathode polarization characteristics were measured at various different temperatures (23, 0, -20 and -40°C).



- ▷ In most cases, the cathode displays poorer kinetics and is performance limiting.

Technique assists in ascertaining the limiting electrode after being subjected to high temperature storage.

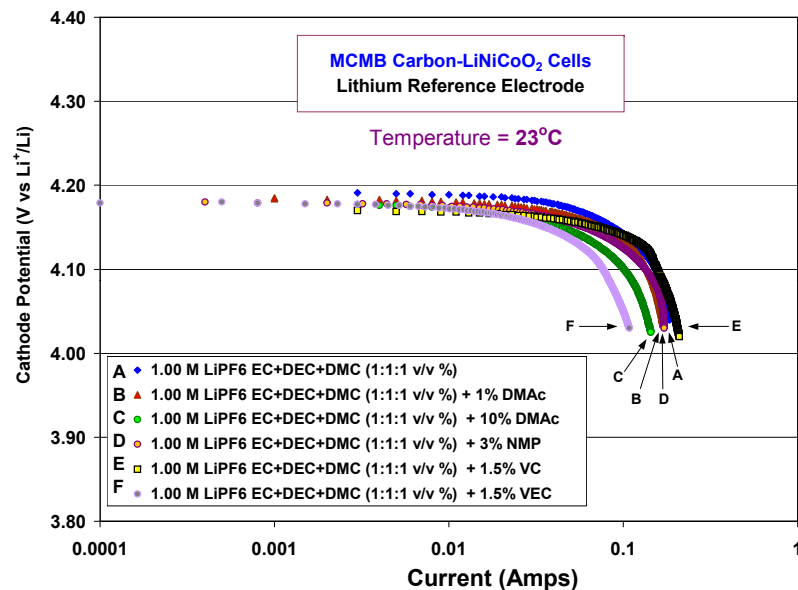




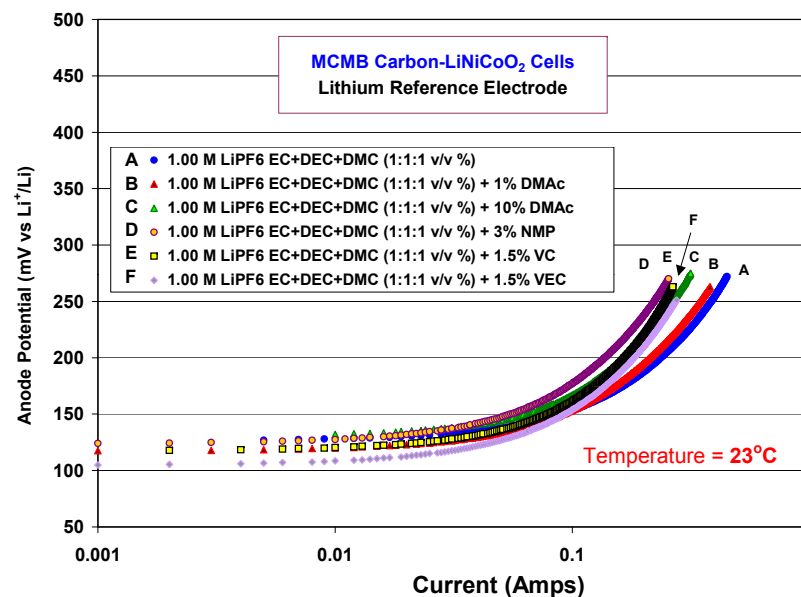
## Performance of High Temperature Resilient Li-Ion Electrolytes

### Tafel Polarization Measurements Prior to High Temperature Storage

#### Cathode Measurements at 23°C



#### Anode Measurements at 23°C



The cell with the baseline electrolyte, **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1)**, exhibited the highest limiting current densities on **MCMB** electrodes prior to high temperature storage testing.

The cell with the **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) + 1.5 % VC** electrolyte exhibited the highest limiting current densities on **LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub>** prior to high temperature storage testing.

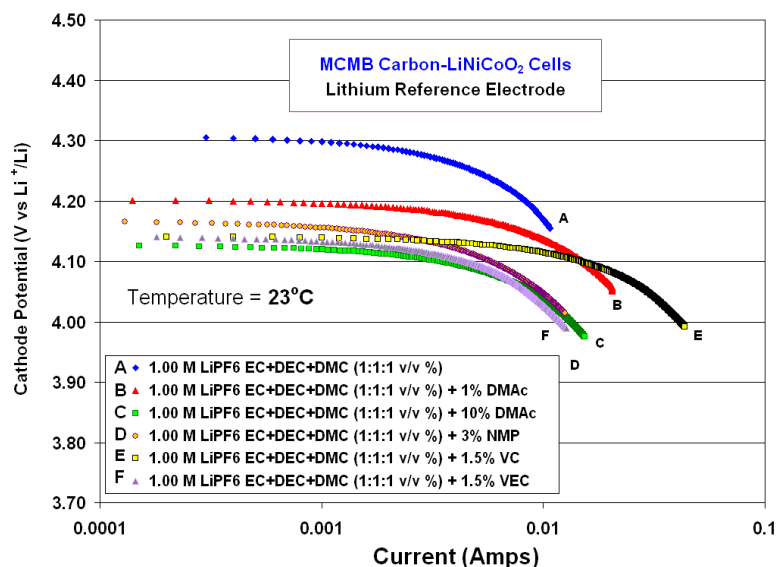


# Performance of High Temperature Resilient Li-Ion Electrolytes

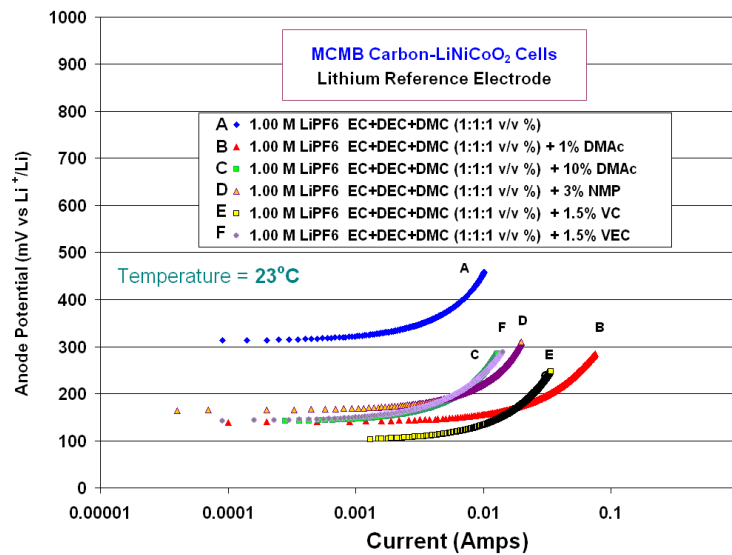
## Results of High Temperature Storage Testing (After 65°C Exposure)

### Tafel Polarization Measurements

#### Cathode Measurements at 23°C



#### Anode Measurements at 23°C



The cell with the **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) + 1.5 % DMAc** electrolyte exhibited the highest limiting current densities on **MCMB** electrodes after being subjected to storage at 65°C.

The cell with the **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) + 1.5 % VC** electrolyte exhibited the highest limiting current densities on **LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub>** electrodes after being subjected to storage at 65°C.

➤ **Measurements after 65°C storage test (10 days)**  
(total high temperature storage time = 30 days).





# Performance of High Temperature Resilient Li-Ion Electrolytes

## Results of High Temperature Storage Testing (After 65°C Exposure)

### Tafel Polarization Measurements

#### Cathode Measurements at 23°C

Temperature = + 20°C							
Condition	Baseline (mA)	1% DMAC (mA)	3% DMAC (mA)	10% DMAC (mA)	3% NMP (mA)	1.5% VC (mA)	1.5% VEC (mA)
Before Storage	59	61	32	59.5	48	64	56.2
One week at 55°C	16.8	11.3	12.3	11.3	13.6	33	11
Additional week at 60°C	6.0	4.9	8.3	6.0	4.9	10.2	6.3
Additional week at 65°C	2.9	4.36	6.9	4.8	2.6	8.7	3.8

Temperature = - 20°C							
Condition	Baseline (mA)	1% DMAC (mA)	3% DMAC (mA)	10% DMAC (mA)	3% NMP (mA)	1.5% VC (mA)	1.5% VEC (mA)
Before Storage	11.2	11.4	4.8	4.9	9.4	27.1	9.7
One week at 55°C	1.6	1.1	0.87	0.5	1.3	5.8	3.1
Additional week at 60°C	1	0.7	0.31	0.3	0.3	2.1	1.0
Additional week at 65°C		0.23	0.21	0.24	0.1	1.1	1.2

#### Anode Measurements at 23°C

Temperature = + 20°C							
Condition	Baseline (mA)	1% DMAC (mA)	3% DMAC (mA)	10% DMAC (mA)	3% NMP (mA)	1.5% VC (mA)	1.5% VEC (mA)
Before Storage	93	67	49	83	54.7	70.6	60.3
One week at 55°C	79	92	67.9	41.4	41	48.3	33.8
Additional week at 60°C	25.1	45	40.5	12	25.7	17	14.3
Additional week at 65°C	2.5	22	24.8	4.3	5.6	9.3	3.5

Temperature = - 20°C							
Condition	Baseline (mA)	1% DMAC (mA)	3% DMAC (mA)	10% DMAC (mA)	3% NMP (mA)	1.5% VC (mA)	1.5% VEC (mA)
Before Storage	22.6	9.1	7.5	7.2	6.8	8.1	9.3
One week at 55°C	13.1	13.9	2.9	2.3	3	4.3	2.9
Additional week at 60°C	0.25	1.3	2.75	0.5	1.8	1.6	1.0
Additional week at 65°C		0.99	1.7	0.13	0.15	0.48	0.25

The cell with the **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) + 1.5 % DMAc** electrolyte exhibited the highest limiting current densities on **MCMB** electrodes after being subjected to storage at 65°C.

The cell with the **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) + 1.5 % VC** electrolyte exhibited the highest limiting current densities on **LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub>** electrodes after being subjected to storage at 65°C.

Similar trends were exhibited at -20°C.

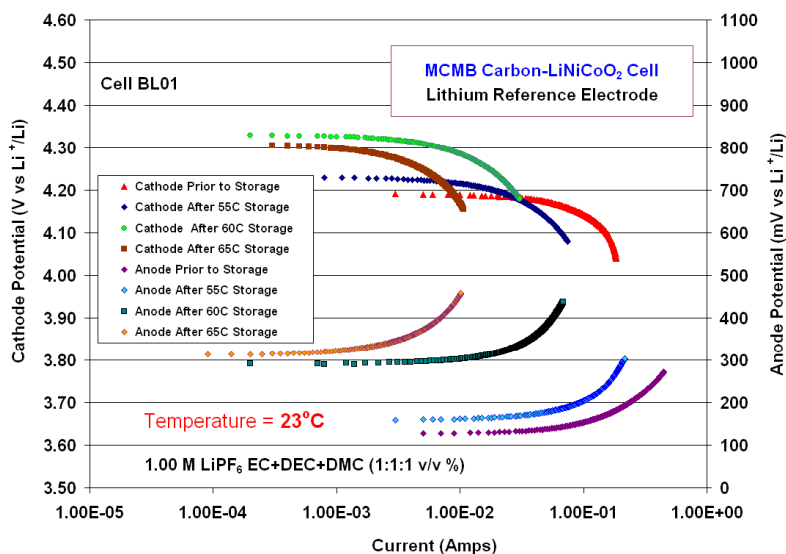


# Performance of High Temperature Resilient Li-Ion Electrolytes

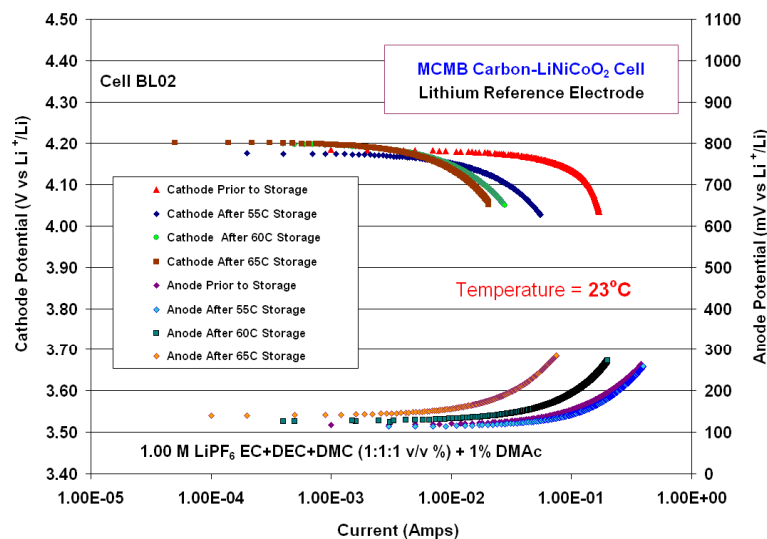
## Results of High Temperature Storage Testing (After 65°C Exposure)

### Tafel Polarization Measurements

➤ **Electrolyte = 1.0 M LiPF<sub>6</sub> in EC+DEC+DMC (1:1:1) (Baseline)**



➤ **Electrolyte = 1.0 M LiPF<sub>6</sub> in EC+DEC+DMC (1:1:1) + 1 % DMAc**



The cell with the **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) + 1.5 % DMAc** electrolyte exhibited the highest limiting current densities on **MCMB** electrodes after being subjected to storage at 65°C.

The cell with the **1.0 M LiPF<sub>6</sub> EC+DEC+DMC (1:1:1) + 1.5 % VC** electrolyte exhibited the highest limiting current densities on **LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub>** electrodes after being subjected to storage at 65°C.

# EIS Measurements of MCMB-LiNiCoO<sub>2</sub> Experimental Cells

## EIS of SEI-Covered Carbon Electrodes

$R_s$  : Electrolyte/Electrode Resistance

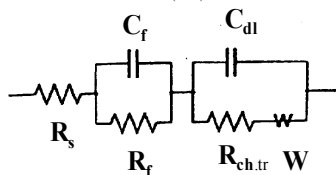
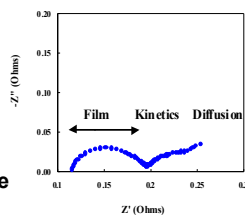
$R_f$  : SEI Resistance

$C_f$  : SEI Capacitance

$C_{dl}$  : Double layer Capacitance

$R_{ch, Tr}$  : Charge Transfer Resistance

$W$  : Diffusional (Warburg) Impedance



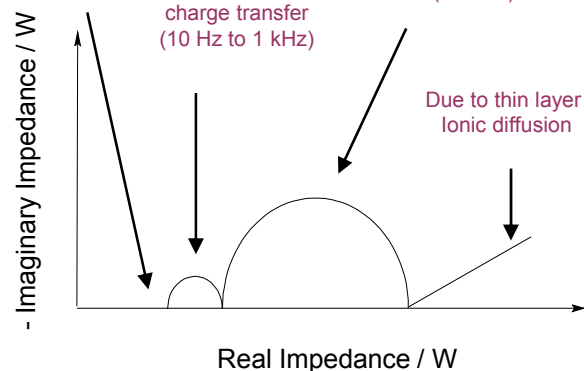
## Interpretation of Li<sub>1-x</sub>Ni<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub> EIS Spectra

Dispersion characteristic of passivating layer (> 1 kHz)

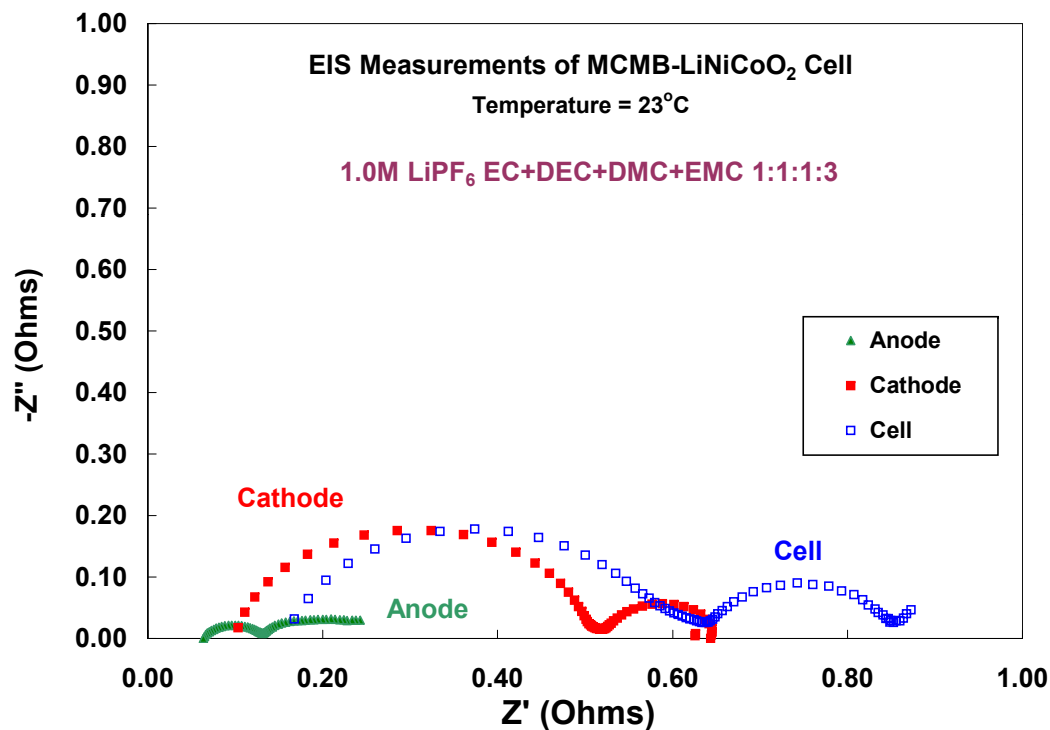
Dispersion characteristic of charge transfer (10 Hz to 1 kHz)

Related to electron transfer (< 1 Hz)

Due to thin layer ionic diffusion



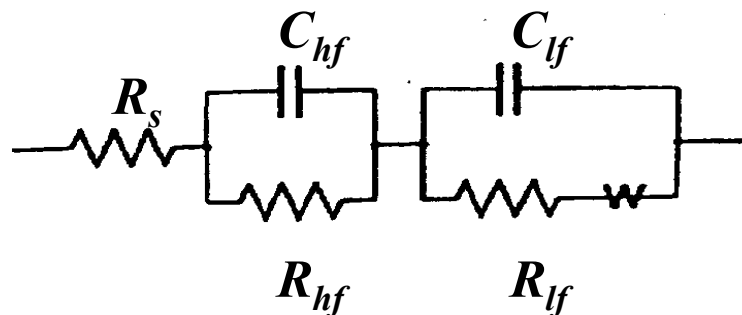
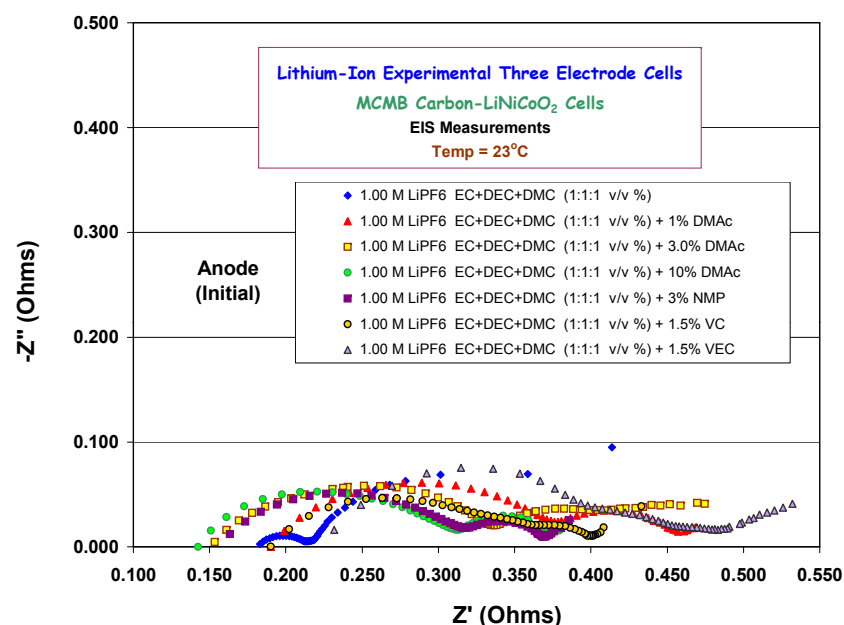
## EIS of MCMB-LiNiCoO<sub>2</sub> Cell Low Temperature Electrolyte



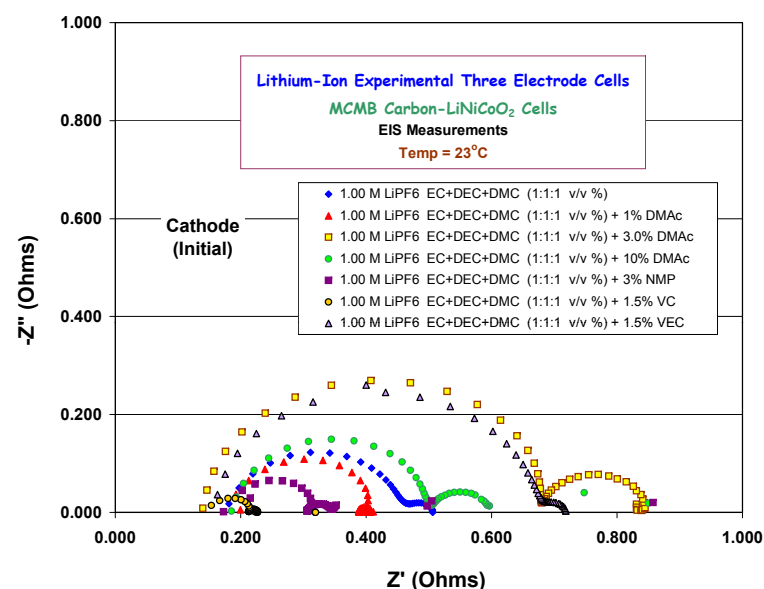
# Performance of High Temperature Resilient Li-Ion Electrolytes

## EIS Measurements Prior to High Temperature Storage

### Cathode Measurements at 23°C



### Anode Measurements at 23°C



➤ The equivalent circuit typically used to interpret an impedance pattern with two relaxation loops is comprised of a series resistance,  $R_s$ , a parallel resistor-capacitor ( $C_{hf}$  and  $R_{hf}$ ) (high frequency relaxation loop), a resistor-capacitor parallel network (low frequency loop) ( $C_{lf}$  and  $R_{lf}$ ) and a Warburg impedance ( $w$ ).

➤ The kinetic parameters of the EIS responses observed for both anode and cathodes were determined as a function of storage period.

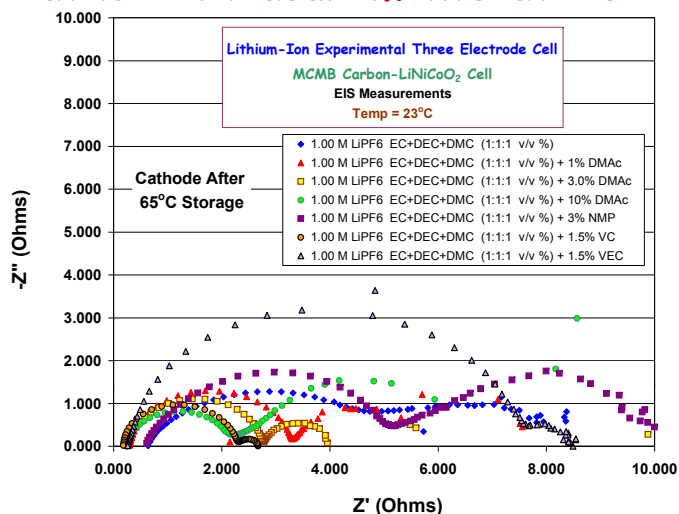




# Performance of High Temperature Resilient Electrolytes

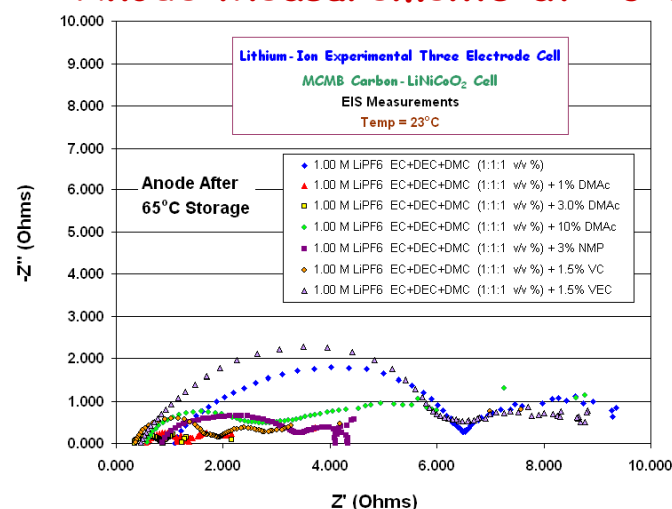
## EIS Measurements After 65°C Exposure

### Cathode Measurements at 23°C



Electrolyte Type	Temperature	SEI parameters			Reaction parameters	
		$R_s$ ( $\Omega$ )	$R_f$ ( $\Omega$ )	$Q_{dl}$	$R_{ct}$ ( $\Omega$ )	$Q_{dl}$
Baseline	Before Storage	0.18	1.04	0.00015	0.26	0.56
	10 days at 55°C	0.37	2.31	0.00027	1.05	0.35
	10 days at 60°C	0.61	4.62	0.102	3.53	0.00089
	10 days at 65°C	0.61	4.62	0.102	3.53	0.00089
1% DMac	Before Storage	0.2	0.2	0.00045		
	10 days at 55°C	0.15	1.66	0.00019	0.48	0.48
	10 days at 60°C	0.27	3.16	0.00019	1.11	0.42
	10 days at 65°C	0.32	2.94	0.00019	1.654	0.33
10% DMac	Before Storage	0.19	0.3	0.00039	0.091	0.83
	10 days at 55°C	0.18	1.25	0.00017	0.8	0.57
	10 days at 60°C	0.23	2.3	0.41	2.1	0.00016
	10 days at 65°C	0.26	6.3	0.32	1.83	0.00029
3% NMP	Before Storage	0.19	0.12	0.00061	0.031	1.69
	10 days at 55°C	0.24	1.33	0.00016	0.57	0.55
	10 days at 60°C	0.36	2.6	0.00017	1.24	0.40
	10 days at 65°C	0.61	5.27	0.19	4.52	0.00034
1.5% VC	Before Storage	0.16	0.058	0.0012	0.012	2.20
	10 days at 55°C	0.14	0.69	0.00028	0.057	1.09
	10 days at 60°C	0.16	1.37	0.00023	0.12	0.690
	10 days at 65°C	0.19	2.1	0.00023	0.38	0.34

### Anode Measurements at 23°C

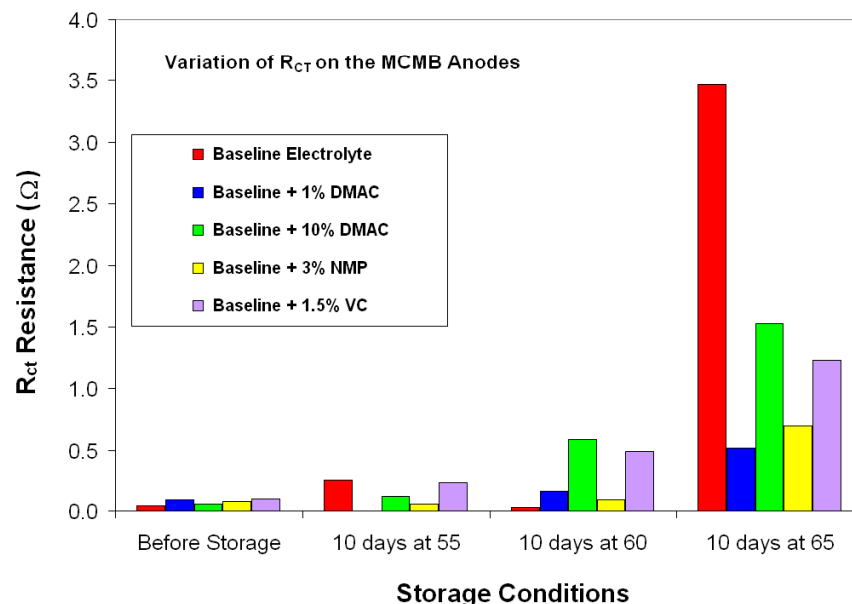
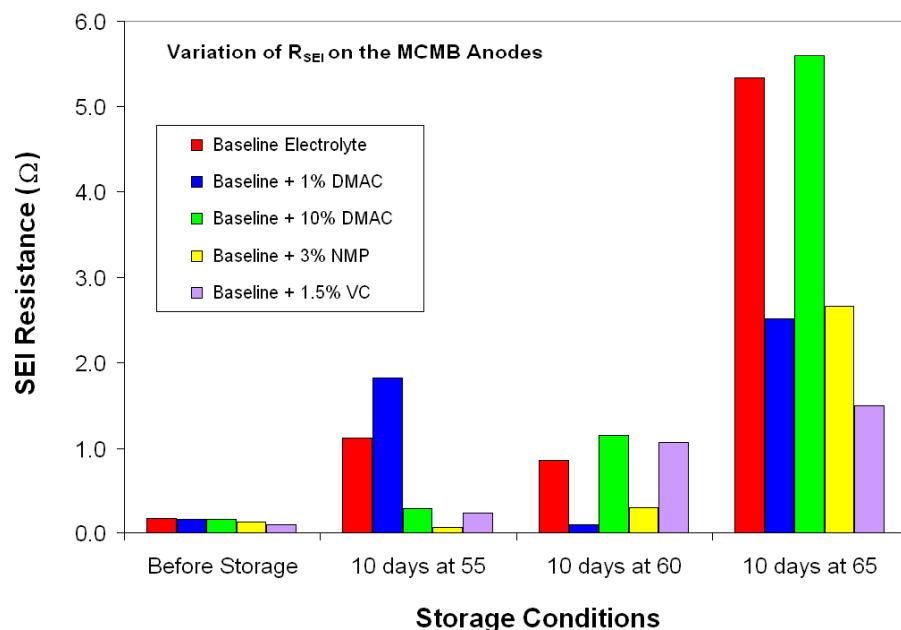


Electrolyte Type	Temperature	SEI parameters			Reaction parameters	
		$R_s$ ( $\Omega$ )	$R_f$ ( $\Omega$ )	$Q_{dl}$	$R_{ct}$ ( $\Omega$ )	$Q_{dl}$
Baseline	Before Storage	0.18	0.17	17.6	0.038	0.29
	10 days at 55°C	0.21	1.12	2.52	0.25	0.11
	10 days at 60°C	0.46	0.86	0.00011	0.027	1.36E-16
	10 days at 65°C	1.22	5.33	0.0022	3.47	0.24
1% DMac	Before Storage	0.2	0.16	0.0059	0.091	1.27
	10 days at 55°C	0.16	1.827	15.7	0.00010	2.80E-08
	10 days at 60°C	0.47	0.091	1.27	0.16	0.0059
	10 days at 65°C	0.61	2.51	3.26	0.52	0.00014
10% DMac	Before Storage	0.15	0.16	0.0079	0.057	1.11
	10 days at 55°C	0.22	0.28	2.7	0.12	0.00058
	10 days at 60°C	0.41	1.15	0.73	0.59	0.00013
	10 days at 65°C	0.55	5.6	0.13	1.53	0.00017
3% NMP	Before Storage	0.17	0.13	0.0036	0.075	1.3
	10 days at 55°C	0.28	0.061	0.26	0.057	0.00121
	10 days at 60°C	0.53	0.29	0.00028	0.087	0.71
	10 days at 65°C	0.79	2.66	0.0015	0.70	0.12
1.5% VC	Before Storage	0.21	0.09	0.0012	0.099	0.36
	10 days at 55°C	0.24	0.23	0.83	0.23000	0.83
	10 days at 60°C	0.28	1.07	1.57	0.49	0.00021
	10 days at 65°C	0.35	1.5	0.3900	1.23	0.00013

# Performance of High Temperature Resilient Electrolytes

## EIS Measurements After High Temperature Exposure

### Anode Measurements at 23°C



The cells containing 1.5% VC and 1% DMAC added to the electrolyte displayed the lowest film and charge transfer resistances, suggesting that they have a beneficial effect in preserving the desirable SEI films on the anode surface, whether by directly being incorporated into the SEI (VC) or by preventing decomposition reaction products from depositing upon the surface (DMAC).





## SUMMARY and CONCLUSIONS

- **High Temperature Resilience of Li-ion electrolytes**

- *It was determined that cells containing electrolytes when compared in terms of the extent of capacity retention observed, the following trend was seen (in decreasing capacity delivered at a  $\sim C/16$  rate at  $20^{\circ}\text{C}$ ): Ternary + 3 % DMAc > Ternary + 1 % DMAc > Ternary + 1.5 % VC > Ternary + 1.5 % VEC > Ternary + 3 % NMP > 1.0M  $\text{LiPF}_6$  EC+DEC+DMC (1:1:1) (baseline).*
- *The degradation of the anode kinetics was slowed most dramatically by the incorporation of DMAc into the electrolytes*
- *The greatest retention in the cathode kinetics was observed in the cell containing the electrolyte with VC added.*
- *Studies are also focused upon determining the high temperature resilience of these solutions in relation to the all carbonate-based mixtures.*

- **Future Work**

- *Studies are currently focused upon determining the high temperature resilience of cells containing electrolytes with different solvent mixtures containing these additives.*
- *Additional effort is being devoted to identifying other promising electrolyte additives.*





# Acknowledgments

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA) and under sponsorship of the NASA-Exploration Systems Mission Directorate (ESRT).

